

PATENT SPECIFICATION

NO. DRAWINGS

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COMPLETE SPECIFICATION

Process for Producing Polyolefin Foams

We, HERCULES INCORPORATED, of Wilmington 99, Delaware, United States of America, a Corporation organised and existing under the laws of the State of Delaware, 5 United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following 10 statement: —

The present invention relates to a process for the production of polyolefin compositions in expanded or cellular form and more particularly to the production of cellular compositions from normally solid polyolefins using 15 a novel blowing agent.

It is well known that polyolefins can be used in the preparation of expanded materials, 20 i.e., foams, by incorporating in the polymer a solid (or liquid) chemical blowing agent which, under the influence of heat, decomposes and evolves gas whereby cells are formed and a low density product is produced. Another process frequently used in the incorporation of a gas in the molten polymer while 25 under pressure followed by the sudden release of the pressure whereby the polymer is expanded.

It has now been found that certain Group 30 I A or II A metal salts which contain water of hydration are also effective blowing agents for polyolefins.

Accordingly, the present invention relates 35 to a process for producing cellular compositions from polymers and/or copolymers of aliphatic olefines which comprises incorporating into the polymer a hydrated salt of a Group I A or II A metal wherein the salt forming anion is selected from the group 40 consisting of phosphate, acid phosphate, hypophosphite, chromate, sulfate, tartrate, acid tartrate, citrate, acid citrate, acetate, lactate, and borate, and heating the resulting mixture

to a temperature sufficient to release the 45 hydrated water as steam and to blow the polyolefin.

Although the hydrated Group I A and 50 II A metal salts of the present invention are very effective blowing agents, an even further increase in expansion of the polymer can be achieved by also incorporating a chemical blowing agent which liberates gas at the 55 temperature employed in the invention such as, for example, azobisisformamide, diazo-aminobenzene, N,N' - dinitrosopentamethylene tetramine, N,N' - dimethyl - N,N' - dinitroso-terephthalamide, p,p' - oxybis(benzenesulfonyl semicarbazide), azobis(isobutyronitrile), p,p' - 60 oxybis(benzenesulfonyl hydrazide), p,p' - di-phenylbis(sulfonyl hydrazide), benzenesulfonyl hydrazide, m - benzenebis(sulfonyl hydrazide) and the like, into the polymer. The use of 65 a mixture of the hydrated salt and a chemical blowing agent represents a preferred embodiment of the invention.

The polymers and copolymers of aliphatic 70 olefines which can be blown in accordance with the invention, include polyethylene and the essentially crystalline polymers of higher mono- α -olefins often referred to as stereoregular polymers or isotactic or syndiotactic polymers. Although any crystalline polymer of an olefin having at least 2 carbon atoms is suitable, the invention is particularly useful for forming cellular compositions of polyethylene, both high and low density types, and isotactic polypropylene. Copolymers of ethylene or propylene with each other or 75 with another monomer can also be used.

The blowing agents used in accordance 80 with the present invention are, as stated above, hydrated salts of Group I A and II A metals wherein the salt forming anion is phosphate, acid phosphate, hypophosphite, chromate, sulfate, tartrate, acid tartrate, citrate, acid citrate, acetate, lactate, 85 and borate. Preferred

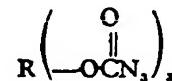
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- salts include the various hydrates of magnesium sulfate such as the dihydrate and the heptahydrate, hydrated calcium sulfate such as the sesquihydrate and the dihydrate, calcium tartrate tetrahydrate, lithium sulfate monohydrate, potassium citrate monohydrate, and potassium sodium tartrate tetrahydrate. Other suitable hydrated salts include magnesium acetate tetrahydrate, magnesium citrate tetradecane hydrate, magnesium acid citrate pentahydrate, magnesium chromate heptahydrate, magnesium hypophosphate hexahydrate, magnesium lactate trihydrate, magnesium phosphate tetrahydrate, magnesium acid phosphate heptahydrate, magnesium pyrophosphate trihydrate, magnesium tartrate pentahydrate, magnesium acid tartrate tetrahydrate, calcium acetate monohydrate, calcium borate dihydrate, calcium chromate dihydrate, calcium citrate tetrahydrate, calcium lactate pentahydrate, calcium hydrogen phosphate tetrahydrate, monocalcium phosphate monohydrate, calcium pyrophosphate tetrahydrate, tricalcium phosphate monohydrate, calcium phosphite trihydrate, lithium acetate dihydrate, lithium borate pentahydrate, lithium chromate dihydrate, lithium citrate tetrahydrate, lithium phosphate monohydrate, lithium tartrate monohydrate, lithium bitartrate monohydrate, hydrated sodium acetate, sodium metaborate tetrahydrate, sodium tetraborate pentahydrate, sodium tetraborate decahydrate, sodium perborate tetrahydrate, sodium chromate decahydrate, sodium dichromate dihydrate, tribasic sodium orthophosphate duodecahydrate, dibasic hydrous disodium orthophosphate duodecahydrate, monobasic monosodium orthophosphate monohydrate, sodium pyrophosphate decahydrate, sodium hypophosphate monohydrate, sodium phosphite pentahydrate, sodium bisulfate monohydrate, normal sodium sulfate monohydrate, normal sodium sulfate heptahydrate, normal sodium sulfate decahydrate, sodium hyposulfate dihydrate, sodium tartrate dihydrate, sodium bitartrate monohydrate, potassium tetraborate pentahydrate, potassium pyrophosphate trihydrate, potassium tartrate sesquihydrate, strontium acetate sesquihydrate, strontium lactate trihydrate, strontium tartrate tetrahydrate, strontium hyposulfate tetrahydrate, barium acetate monohydrate, barium borate heptahydrate, barium citrate heptahydrate, barium hypophosphate monohydrate, barium hyposulfate dihydrate, barium persulfate tetrahydrate, barium tartrate monohydrate, beryllium sulfate tetrahydrate, beryllium sulfate heptahydrate, and the like.
- The proportion of hydrated salt employed as blowing agent can vary over a wide range depending on the nature and characteristics of the salt and the extent of expansion of the product which it is desired to obtain. In general, an amount ranging from 0.1% to 20% by weight of the polyolefine and prefer-

ably from 1% to 10% will be sufficient to form light cellular products. As stated above, the hydrated salts of the invention can also be used in mixture with chemical blowing agents. The chemical blowing agent when employed will usually be present in an amount equal to from 0.1% to 10% of the mixture and preferably from 0.1% to 3%.

The polyolefin may also contain other materials such as stabilizers, cross-linking agents, and the like. The use of an azido cross-linking agent in addition to the blowing agent is preferred for the production of cellular polyolefin compositions having densities as low as 20 lbs./cu. ft. since its use enables one to obtain a finer and more uniform cell structure and a much higher percentage of closed cells. The preferred azido cross-linking agent for use in the invention is a poly(sulfonazido), i.e., any compound having the general formula $R_x(SO_2N_3)_x$, where R is an organic radical inert to the cross-linking reaction and x is an integer greater than 1. Preferably, x will be an integer from 2 to 100 and R will be selected from the group of organic radicals consisting of alkylene, arylene, aralkylene, and alkarylene radicals; however, these radicals can also contain ether, alcohol, halogen groups which are inert to the cross-linking reaction. Exemplary of the poly(sulfonazido)s that can be used are 1,7 - heptane - bis(sulfonazido), 1,9 - nonanebis(sulfonazido), 1,10 - decanebis(sulfonazido), 1,11 - undecane - bis(sulfonazido), 1,12 - dodecanebis(sulfonazido), 7-octadecane - 1,13 - bis(sulfonazido), 6-thiaundecane - 1,11 - bis(sulfonazido), chloroaliphatic poly(sulfonazido)s such as the poly(sulfonazido) produced from a chloro- and sulfochlorinated mixture of petroleum hydrocarbons containing at least one chlorine atom and at least two sulfonazido groups per molecule, 1,9 - 18 - octadecane - tris(sulfonazido), poly(ethylene sulfonazido), poly(sulfonazido-methylstyrene), 1,3- and 1,4 - bis(sulfonazido-methylbenzene), 1,3 - benzene - bis(sulfonazido), 1 - octyl - 2,4,6 - benzene - tris(sulfonazido), 4,4' - diphenylmethane - bis(sulfonazido), 4,4 - diphenylether - bis(sulfonazido), 4,4' - bis - octadecyl biphenyl-3,5,3',5' - tetra(sulfonazido), 4,4' - diphenyl-disulfide - bis(sulfonazido), 1,6 - bis(4'-sulfonazidophenyl) hexane, 2,7 - naphthalene-bis(sulfonazido).

Another class of azido cross-linking agents that can be used are polyazidoformates which have the general formula



where x is at least 2, preferably from 2 to 4, and R is an organic radical, inert to cross-linking reactions, containing at least

one carbon atom per azidoformate group. Exemplary of these azidoformates are those compounds where R is alkylene, as for example in ethylene-bis(azidoformate), tri-methylene 1,3 - bis(azidoformate), tetra-methylene - 1,4 - bis(azidoformate), penta-methylene 1,5 bis(azidoformate), hexa-methylene - bis(azidoformate), 1,9 - nonane-bis(azidoformate), 1,10 - decane - bis (azidoformate), cyclo - alkylene, as for example in cyclohexylene - 1,2 - bis(azidoformate), cyclohexylene 1,3 bis(azidoformate), and cyclohexyl - 1,4 - bis(azidoformate); arylene, as for example in *o*-, *m*-, and *p*-phenylene bis(azidoformate); arylene - dialkylene, as for example in *o*-, *m*-, and *p*-xylylene - bis(azidoformate); alkylene - diarylene, as for example in 2,2' - isopropylidene - bis(*p,p'* - phenyl-azidoformate); cycloalkylene - dialkylene, as for example in 1,4 - cyclohexane - dimethyl-bis(azidoformate); oxydialkylene, as for example in 2,2' - oxydiethyl - bis(azidoformate), 2,2' - oxydipropyl - bis(azidoformate); thiobis-dialkylene, as for example in 2,2' - thiobis-ethyl - bis(azidoformate), 4,4' - thiobisbutyl-bis(azidoformate); alkylene poly(oxyalkylene), as for example in 2,2' - ethylenedioxyethyl-bis(azidoformate), i.e., ethylene - bis(oxyethylene azidoformate), the tris(azidoformate) 30 of glycerol-propylene oxide adduct; alkylene-bis(polyoxyalkylene), as for example the bis(azidoformate)s of poly(ethylene glycol) and poly(propylene glycol), and carbonyl tetrakis-(alkyleneoxyalkylene), as for example the tetraazidoformate of pentaerythritol-propylene oxide adduct.

The amount of the azido cross-linking agent utilized can be varied over a wide range and will depend upon the type of azido cross-linking agent used, the polymer being foamed, the properties desired in the final foam, and, if employed, should be an amount sufficient to prevent rupture of the cell walls when the foaming action takes place. Generally, an amount of from 0.001% up to 5% or more, and preferably from 0.005% to 2%, and more preferably from 0.08% to 2% by weight of the polymer will be sufficient. Depending upon the amount and type of azido cross-linking agent used, actual cross-linking of the polymer may or may not occur. Thus, for example at low levels of polysulfonazides, particularly those of high molecular weight, there will be an insufficient amount to achieve actual cross-linking (insolubilization of the polymer), yet the polymer will be modified to such an extent that collapse of the cell walls is prevented, which collapse would occur if no azido cross-linking agent were used. Larger amounts of the azido cross-linking agent will be used when a cross-linked, foamed product is desired.

The process of the invention is suitably carried out by mixing the aliphatic olefin polymer or copolymer with the blowing agent,

and any other desired components such as plasticizers, fillers, stabilizers, cross-linking agents, and the like, in conventional manner and then heating the mixture to a temperature sufficiently high to release the water of hydration to generate steam and at least to 70 Temperatures in the range of 120° C. to 240° C. are usually sufficient, but the temperature varies slightly with the polyolefin to be blown. The period of time required to effect the desired degree of blowing will depend on the temperature used, but usually will be about 1 to 10 minutes. The exact 75 temperature to be used will then depend on the blowing agents used, whether or not cross-linking agents and other blowing agents are present, the softening point of the polymer and the length of time the mixture is heated. The expandable composition can be heated 80 in any desired fashion as, for example, in a mold or open vessel, or in an extruder. A particularly suitable method is to charge the mixture to a mold which is then closed and heated, under pressure if desired, to a 85 temperature sufficiently high to melt the polymer and to decompose the hydrated salt and release its water of hydration as steam, after which the mold is opened to allow the polymer to expand into a cellular composition. The 90 cellular composition is then cooled and removed from the mold.

By the employment of the present invention it is possible to obtain an expanded product of low density in a process which can be simply controlled and which is readily reproducible. One of the advantages attendant upon the employment of the present invention includes the fact that the hydrated salts of this invention are inexpensive blowing agents which can be advantageously used in place of all or part of the more expensive materials.

The invention will be illustrated by the following examples in which all parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

In this example 100 parts of stereoregular polypropylene having a birefringent melting point of about 168° C., a reduced specific viscosity of 3.2 (measured as a 0.1% solution in decahydronaphthalene at 135° C.) and a melt index (I_2 , 230° C.) of 4.0 and containing 0.5% of 1,10 - decane - bis(sulfonazide) as cross-linking agent and 0.5% of 4,4' - thiobis(3 - methyl - 6 - tert - butylphenol) as stabilizer was thoroughly blended with 6 parts of magnesium sulfate heptahydrate on a 2-roll mill for 5 minutes at 115 180° C. The blend was removed from the mill as an 1/8-inch thick sheet which was cooled and then chopped into 1/4-inch 120 granules. Eighty-two parts of the granules were placed in a 5 inch×5 inch×0.25-inch 125 mold and the mold was closed tightly and 130

held in an hydraulic press heated to 216° C. for 6 minutes after which the press was opened rapidly to allow expansion of the foam from the mold, and the foam was cooled under an aluminum plate at an applied pressure of less than 0.1 p.s.i. There was obtained a cellular product having a density of 21 lbs./cu.ft. A molding prepared from granules of polypropylene which contained no magnesium salt gave a product having a density of 36 lbs./cu.ft.

EXAMPLE 2

The procedure of Example 1 was repeated exactly as described above except that 4.5 parts of magnesium sulfate heptahydrate and 0.58 part of azobisformamide were substituted for the 6 parts of magnesium sulfate heptahydrate of Example 1. The cellular product had uniform closed cells and had a density of 13 lbs./cu.ft.

EXAMPLE 3

The procedure of Example 2 was repeated except that 1.28 parts of azobisformamide was used instead of 0.58 part of azobisformamide. The product of this example had a density of 10 lbs./cu.ft.

EXAMPLES 4—5

The procedure of Example 3 was repeated using 5.0 parts of calcium tartrate tetrahydrate (Example 4) or 5.0 parts of calcium sulfate sesquihydrate (Example 5) instead of 4.5 parts of the magnesium sulfate heptahydrate. The cellular products contained fine uniform cells which were predominantly closed and had densities of 9.3 and 11.9 lbs./cu.ft., respectively.

EXAMPLE 6

In this example 100 parts of polyethylene flake having a density of 0.945 g./cu.cm., and a melt index (I_2 , 190° C.) of 0.2 and containing 0.5 % of 4,4' - thiobis(3 - methyl-6 - tert - butyl - phenol) as stabilizer was thoroughly blended with 0.50 part of magnesium sulfate heptahydrate, 2.30 parts of

azobisformamide, and 1.0 part of 1,10-decanbis(sulfonazide) in a ball mill. The blend was next extruded into molding powder at 154° C., and the molding powder converted into a cellular product according to the procedure described in Example 1 except that the mold was heated at 200° C. for 6 minutes. The cellular product had a density of 5.75 lbs./cu.ft. A product prepared from polyethylene flake in the same way as above except that no magnesium salt was employed had a density of 10.0 lbs./cu.ft. Repetition of the process of this example except that the amount of azobisformamide was reduced to 0.58 part and the magnesium sulfate heptahydrate was reduced to 0.45 part gave a product having a density of 9.5 lbs./cu.ft.

EXAMPLES 7—9

In each of these examples 100 parts of stereoregular polypropylene having a birefringent melting point of about 168° C., a reduced specific viscosity of 3.2, and a melt index (I_2 , 230° C.) of 4.0, 0.5 part of 4,4' - thiobis(3 - methyl - 6 - tert - butylphenol) as stabilizer, 1.5 parts of magnesium sulfate heptahydrate which had previously been ball-milled to a fine particle size, from 0 to 0.01 part of tetramethylene - 1,4 - bis(azidoformate) as cross-linking agent, and 150 parts of acetone were thoroughly slurried at room temperature until an intimate dispersion was obtained, after which the slurry was dried in a steam oven at 60° C. Each of the dry compositions was then extruded on a 3/4-inch 20:1 (length : diameter) extruder fitted with a conventional metering screen and an 1/8-inch circular hole die under the following conditions:

Extruder barrel temperature	204°C.
Die temperature	180°C.
r.p.m.	50

The amount of tetramethylene-bis(azidoformate), i.e., TBAF, used in the compositions of these examples and the density of the extruded rod so produced are recorded below in Table I.

Table I

Example	TBAF (parts by weight)	Density (lbs. per cu.ft.)
7	0	19.6
8	0.005	11.7
9	0.01	12.6

EXAMPLES 10—13

In these examples 100 parts of the stereoregular polypropylene of Examples 7—9, 0.5 part of 4,4' - thiobis(3 - methyl - 6 - tert - butylphenol), 0.5 part of 1,9 - nonanabis(sulfonazide), and 8 parts of a hydrated salt were ball-milled for 2 hours and then slurried

with 150 parts of acetone and dried as in Examples 7—9. Eighty-two (82) parts of the dry compositions were then placed in 4 inch × 4 inch × 1/4-inch picture frame molds and converted into cellular products in accordance with the procedure of Example 1. Compositions of these examples with respect to the

hydrated salt and densities of the cellular products obtained, as compared with a control prepared in the same manner except that the hydrated salt was omitted are recorded in Table II below.

Table II

Example	Hydrated Salt	Density (lbs./cu.ft)
10	$\text{LiSO}_4 \cdot \text{H}_2\text{O}$	8.1
11	$\text{K}_2\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$	16.0
12	$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	14.5
13	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	10.2
Control	—	44.5

WHAT WE CLAIM IS:—

- 15 1. A process for producing cellular compositions from polymers and/or copolymers of aliphatic olefins which comprises incorporating into said polymer a hydrated salt of a metal selected from the group consisting of Group I-A and Group II-A metals wherein the salt-forming anion is selected from the group consisting of phosphate, acid phosphate, hypophosphite, chromate, sulfate, tartrate, acid tartrate, citrate, acid citrate, acetate, lactate, and borate, and heating the resulting mixture to a temperature above the softening temperature of the polyolefin and sufficient to release the water from said hydrated salt and to expand the polyolefin to produce a cellular composition.
- 20 2. A process according to Claim 1 in which a chemical blowing agent is also incorporated into said polyolefin.
- 25 3. A process according to Claim 1 or Claim 2 wherein the mixture also contains an azido cross-linking agent.
- 30 4. A process according to any of the preceding claims wherein the polyolefin is polypropylene.
- 35 5. A process according to any of claims 1 to 3 wherein the polyolefin is polyethylene.
- 40 6. A process according to any of the preceding claims wherein the hydrated salt is magnesium sulfate heptahydrate.
- 45 7. A process according to any of Claims 1 to 5 wherein the hydrated salt is calcium sulfate sesquihydrate.
- 50 8. A process according to any of Claims 1 to 5 wherein the hydrated salt is calcium tartrate hydrate.
- 55 9. A process according to any of Claims 1 to 5 wherein the hydrated salt is lithium sulfate monohydrate.
- 60 10. A process according to any of Claims 1 to 5 wherein the hydrated salt is potassium sodium tartrate tetrahydrate.
- 65 11. A process according to any of Claims 1 to 5 wherein the hydrated salt is potassium citrate monohydrate.
- 65 12. A process substantially as claimed in claim 1 with particular reference to the accompanying examples.
- 65 13. Cellular polyolefin compositions whenever prepared by a process according to any of the preceding claims.

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